Abstract

The liquid crystal state (mesophase) is designated as a new state of matter as it occurs on the phase diagram between the crystal and the liquid phase. These polymers exhibit properties similar to liquids (fluidity) and solids (molecular order). They are able to undergo a self organisation i.e they align in melt (thermotropic) or in solution (lyotropic) to form domains of microscopic dimensions with the preferential order. One of the major objectives in the design of main chain thermotropic liquid crystalline polymers (MCTLCP) is reduction of the transition temperature into useful working range without destroying the mesophase stability. This can be achieved by one or more combinations of following : i) introducing linking groups having some flexibility between the rigid units, ii) introduction of disrupters (flexible spacer or rigid kinks) into the straight polymer chain, iii) substitution on the mesogenic core, and iv) copolymerisation i.e. different units can be randomly positioned along the chain. The high degree of molecular orientation and order lead to materials with superior tenacity and impact strength when processed from liquid crystalline melt. Liquid crystalline polymers also have a very low coefficient of thermal expansion and unusually high thermal conductivity in the orientation direction. An additional advantage is the lower melt viscosity of liquid crystalline state vis-a-vis isotropic state which originates from molecules sliding past another within domains as well as from domain-domain motion. In turn this property makes these materials highly shear dependent. This aptness of liquid crystallinity can be coupled with another class of polymers known as segmented thermoplastic copoly(ether-ester) elastomers by replacing the crystalline hard segments with liquid crystalline segments. Thermoplastic elastomers are comprised of alternating hard and soft or rubbery segments. At use temperature the lower glass transition, Tg of soft blocks imparts elastomeric properties while rigid hard blocks serve as physical crosslinks and reinforcement sites which are responsible for mechanical performance. The ultimate properties of segmented copoly(ether-ester)s are dependent on chemical composition of hard/ soft blocks and their respective lengths or molecular weights. Above the melting/ glass transition temperature of hard segments, thermoplastic elastomers can be processed similar to conventional thermoplastics. However, incompatibility between hard and soft segment blocks in thermoplastic elastomers results in higher melt viscosity generating difficulties while processing. Replacing thermoplastic hard blocks with liquid crystalline hard blocks will result in polymers which can be easily processed due to their lower viscosity. This generates a new class of materials termed as thermotropic liquid crystalline elastomers. Due to the presence of hard, rigid thermotropic liquid crystalline segments and hence enhanced rate of crystallisation, these copolymers will be amenable to quicker processing and facilitate operations such as short cycle injection molding. In addition, the advantages of above said polymers arise from unusual properties originating from the combination of rubber like elasticity coupled to the directional properties of the mesogen. As a consequence, the exciting prospect is that a liquid crystalline elastomer enables stress field to be coupled into other fields (electric/ magnetic) through molecular orientation effects so as to produce a very large stress-optical effect. Synthesis, characterisation and properties of number of side chain thermotropic liquid crystalline elastomers are reported. However, field of main chain thermotropic liquid crystalline elastomers is just emerging and very few references are cited till date. This thesis encompasses synthesis and characterisation of such new class of main chain thermotropic elastomers. Series of random copoly(ether-ester) elastomers were synthesised by employing combination of purified monomers such as terephthalic acid, rigid diols viz. hydroquinone, methyl hydroquinone, chloro hydroquinone and flexible spacer viz. poly(oxy

ethylene) glycol and poly(oxy butylene) glycol of varying number average molecular weight (250, 650, 1000, 2000). Copoly(ether-ester)s were synthesised via sequential high temperature melt condensation of acid chloride with flexible spacer and rigid diol. Some polymers were synthesised by all together addition of monomers (acid chloride/ flexible spacer/ rigid diol) and their properties were compared with corresponding sequential addition reaction products. Some polymers were also synthesised by employing room temperature solution polycondensation reaction and their properties were compared with melt condensation products with same molar ratios of reactants. Properties of all purified copolymers were studied with respect to following structural variations: a) variation in composition of poly(oxy ethylene) glycol, b) change in type of flexible spacer from poly(oxy ethylene) glycol to poly(oxy butylene) glycol, c) variation in composition of poly(oxy butylene) glycol i.e. change in hard segment length at constant soft segment length, d) variation in molecular weight of poly(oxy butylene) glycol i.e. simultaneous change in hard and soft segment length, e) incorporating lateral substituent in hard segment core, f) changing the polarity of lateral substituent (methyl to chloro), g) replacing part of hydroquinone with methyl or chloro hydroquinone i.e. employing mixture of rigid diols. Solubility study of all the copoly(ether-ester)s was conducted by using common organic solvents such as chlorinated hydrocarbons, aprotic solvents and caustic solvents such as 4-chloro phenol and trifluoroacetic acid. Intrinsic viscosity of soluble copolymers was determined. Formation of ester bond after copolymerisation was characterized by infra-red spectral measurements. Segmented nature of copoly(ether-ester)s were inferred from differential scanning calorimetry (DSC) thermograms through the observations of low temperature glass transition temperature pertaining to soft segment and high temperature glass transition/ melting endotherm corresponding to hard segment. Change in heat capacity and change in enthalpy corresponding to these transitions were related to structural variables. Liquid crystalline phases of the copoly (ether-ester)s, as nematic and smectic, were also identified by optical polarizing microscope (PM) by inspecting the textures at various temperatures. Attempt was also made to recognize the onset of isotropisation of liquid crystalline copoly(ether-ester)s. Percent crystallinity of synthesised copoly(ether-ester)s was determined by using room temperature wide angle x-ray diffractometry. Some copolymers were also investigated by high temperature x-ray diffraction in order to identify crystalline/ liquid crystalline subphases and correlated with results of DSC and PM. Crystallisation kinetic studies of the selected copoly(ether-ester)s was carried out with DSC and Avrami exponent obtained were discussed in relation to variation in composition and nature of reactants.